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Hagen, Anke; Chen, Ming; Neufeld, Kai; Liu, Yi-Lin

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Effect of Humidity in Air on Performance and Long-Term Durability of SOFCs

A. Hagen, M. Chen, K. Neufeld, Y. L. Liu

Risoe DTU, National Laboratory for Sustainable Energy
Frederiksborgvej 399, DK-4000 Roskilde, Denmark

Anode supported SOFCs based on Ni-YSZ anodes, YSZ electrolytes, and LSM-YSZ cathodes were studied with respect to durability in humid air (~4%) over typically 1500 hours. Operating temperature and current density were varied between 750 and 850°C and 0.25-0.75 A/cm², respectively. It was found that the introduction of humidity affected the cell voltage under polarization of the cell and that this effect was (at least partly) reversible upon switching off the humidity, probably related to a segregation of impurities towards the three phase boundary in the presence of humidity. Generally, the studied cells were successfully operated in humid air under technologically relevant conditions. Improvements at the cathode/electrolyte interface made it possible to obtain highly stable cells, which can be operated under high current density and at 750°C in humid air - conditions that are known to cause significant cell voltage degradation in dry air.

Introduction

Performance, durability, and costs are crucial aspects for the success of SOFC technology. Detailed study of the initial performance and degradation mechanisms under relevant operating conditions and at different levels – from materials to stacks and systems – is required to develop a competitive SOFC technology. For application of SOFCs, real operating conditions also comprise impurities in the supplied gasses, such as for example sulphur compounds in the fuel or humidity in air. Humid air has been considered previously mainly in relation to interconnects and Cr-poisoning phenomena (e.g., (1-3)). In this contribution, single, anode supported cells with LSM/YSZ cathodes, YSZ electrolytes, and Ni/YSZ anodes were studied over operating periods between 500 and 2500 hours with regard to the effect of humidity of air. The parameters current density and temperature were varied. The study comprised a detailed micro-structural analysis of the tested and reference cells, as well. Air was humidified by leading it through a water flask at room temperature, giving a humidity of ~4%.

Experimental

Solid Oxide Fuel Cells (SOFCs)

Anode supported SOFCs manufactured at the Risoe pre-pilot laboratory were used. These cells were based on a supporting and active Ni-YSZ cermet anode, a YSZ

electrolyte, and a LSM-YSZ composite cathode. The active area was $4 \times 4 \text{ cm}^2$ (4). For the so-called standard cells, the layers were deposited by tape casting of the anode support and spraying of anode, electrolyte, and cathode. The same half-cells were used in another cell series, where the LSM-YSZ cathode was deposited by a screen printing process.

Testing Equipment

The electrochemical and aging tests were performed in alumina test-houses placed in furnaces and equipped with current and voltage probes, thermo couples, and gas lines. pO_2 sensors were placed at the fuel inlet and outlet tubes. The cells were sandwiched between ceramic gas distribution layers (Ni containing on the anode and LSM containing at the cathode side, respectively) and current collectors (nickel and gold foils at the anode and cathode side, respectively). Seals consisting of glass ceramic composite were placed around the anode and cathode side of the cells. The test set-up and method is described in detail in (5).

Testing Protocol

The cells were first sealed and reduced at 1000°C . Afterwards, the temperature was lowered to start the initial electrochemical characterization at 850, 800, and 750°C (iV curves and impedance spectra: Solartron SI 1260 impedance analyzer in 4% and 20% humidified hydrogen). The same characterization was also performed after completion of the aging tests. Long-term testing was carried out at 850, 800, and 750°C and different, constant current loads. The fuel gas was a mixture of CO_2 and hydrogen with a ratio of 1 to 4, yielding an equilibrium mixture of $\text{CO}:\text{H}_2:\text{H}_2\text{O} = 1:1:4$; this corresponds to a steam to carbon ratio of two. The fuel utilization was adjusted to lie between 75 and 85%. Air was used as cathode gas, both dry and humidified. Dry air contained $\leq 0.1\%$ H_2O . The humidification was accomplished by leading air through a water flask at room temperature, yielding a degree of humidification of ca. 4%.

Micro-structural Analysis

For the microstructural analysis of the cathode/electrolyte interface, a FEG-SEM Supra-35 was used (sample not coated, accelerating voltage 2 kV, secondary detector). The cathode layer was removed by treatment of the cell in concentrated hydrochloric acid in an ultrasonic bath at room temperature for a few minutes. Subsequently, the sample was cleaned in water and ethanol. YSZ and $\text{La}_2\text{Zr}_2\text{O}_7$ are stable in HCl whereas LSM is dissolved. To identify possible reaction products in the interface region, various EDS techniques (point analysis and line scan) with high or low accelerating voltage were used.

Results and Discussion

Initial Electrochemical Characterization

In Table I the initially measured area specific resistance values (ASR) are listed for the cells to be tested in dry or humid air. All cells performed equally well within a small range of variation ($0.19 \pm 0.03 \text{ } \Omega \cdot \text{cm}^2$).

TABLE I. Cell tests, initial ASR* values at 850°C, conditions for long-term testing (aging)

Test ID	ASR _{ini} at 850°C ($\Omega\cdot\text{cm}^2$)	T_{aging} (°C)	%H ₂ O on cathode	i (A/cm ²)
2test46	0.16	750	~4	0.25
12test32	0.19	750	~4	0.41
2test50	0.20	750	~4	0.75
12test33	0.16	750	~4	0.75
13test57 [#]	0.15	750	~4	0.5
5test34	0.21	800	~4	0.5
2test47	0.20	850	~4	0.25
12test35 [□]	0.21	750	~4	0.5
14test7	0.22	750	<0.1	0.25
12test8	0.25	750	<0.1	0.41
13test5	0.17	750	<0.1	0.75
2test16	0.19	750	<0.1	0.75
4test22	0.18	750	<0.1	0.75
12test29	0.22	750	<0.1	0.75
1test31	0.20	850	<0.1	0.25
Average: 0.19±0.03				

* Area specific resistances, determined from iV curves, corrected for fuel utilization

[#] The air utilization was 50% during the aging period in humid air, prior to this period, the cell had been tested for 1800 hours in dry air

[□] Cell with optimized cathode, the air utilization was 70% during the aging period in humid air, prior to this period, the cell had been tested for 2300 hours in dry air

Immediate Effect of Humidification of Air

In the current study, aging tests over 1500 hours were performed at three temperatures and furthermore at four current densities at 750°C to cover ranges dominated by anode or cathode degradation as well. Typically, the aging tests were initiated in dry air and after a period of ~24-48 h, the air was humidified. After additionally 1500 hours (or shorter, depending on the degradation rate), the humidification was stopped and the test completed in dry air, followed by a final electrochemical characterization at OCV.

In Figure 1, a typical cell voltage behavior is shown for the test at 800°C and 0.5 A/cm². The humidification of air had an immediate effect on the cell voltage; it dropped fast. Afterwards, a more constant cell voltage degradation was observed. When stopping the humidification and returning to dry air, the cell voltage increased fast (jump) back to a lower cell voltage than the one at the start of the humidification. The magnitude of the initial cell voltage drop and final cell voltage jump was evaluated in relation to the applied current density. In Figure 2, the cell voltage changes were plotted as a function of the cell polarization (η_{cell} [emf-U]). At OCV, the cell voltage did not change when the degree of humidification of cathode gas was changed from ~0.1 to 4%. With increasing the current density and thus cell polarization, the magnitude of the cell voltage drops (and jumps when returning to dry air) increased. Impedance spectra revealed that this drop, i.e. increase of resistance, was due to a simultaneous increase of both serial and polarization resistances (see Figure 3). The same trend continued during the period under humid air. The frequency region mainly affected by the change of the degree of humidity in air was around 18 kHz.

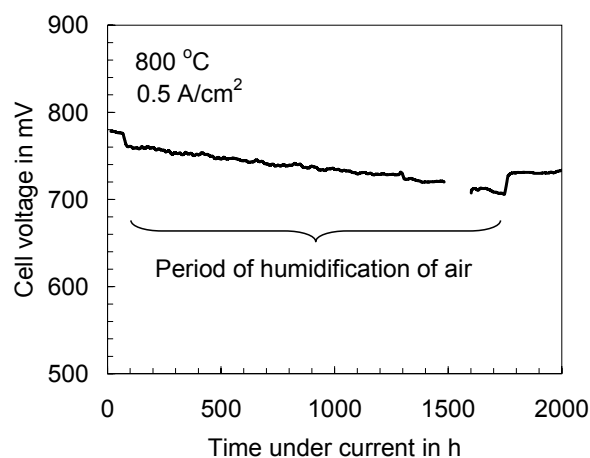


Figure 1. Cell voltage in 5test34, 800°C, 0.5 A/cm², 80% fuel utilization, 10% air utilization, 4% humidity in air during the marked period.

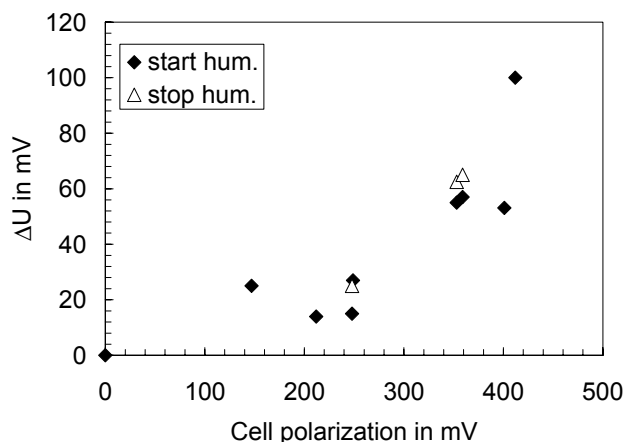


Figure 2. Cell voltage drop and jump during start and stop of humidification of cathode air, respectively (ΔU) as function of cell polarization.

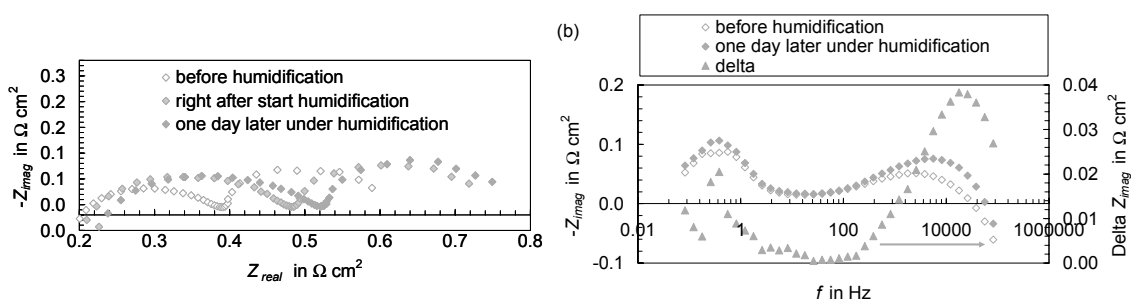


Figure 3. Impedance spectra recorded under current load in 2test50 (see Table I) at 750°C and 0.75 A/cm² just before starting the 4% humidification of air, right after start and after one day in humid air, a) Nyquist, b) Imaginary part vs. frequency and difference between under humidification and before (delta).

Long-Term Effect of Humidification of Air

Results from previous aging tests in dry air (6) were used as references. In this durability study over typically 1500 hours it was found that the cell voltage degradation

increased with increasing current density / cell polarization, in particular at lower operating temperatures of 750 vs. 850°C. The degradation at 750°C was mainly related to cathode processes. The long-term effect of ~4% humidity in air was studied for a series of cells over usually 1500 hours at 850, 800, and 750°C at different current densities. As a measure of degradation, the linear cell voltage degradation over the whole aging period was determined (see also (6)). In Figure 4, these values are plotted as function of the cell polarization and compared to the reference tests in dry air. At a higher operating temperature of 850°C and 0.25 A/cm², the cell voltage degradation rates were zero mV/1000 h for the test in dry air and 8 mV/1000 h in humid air. The cell voltage was thus hardly affected by introduction of ~4% humidification of air.

At 750°C, the cell voltage degradation rate was larger compared to the operation in dried air under the same current load / cell polarization. Furthermore, it increased with increasing cell polarization (see Figure 4). The tests at 800°C gave a similar trend as the tests at 750°C (square in Figure 4). The cell polarization seems thus to have a larger effect on the cell voltage degradation rate than the temperature in the range between 800 and 750°C. The effect of humidification of air on the cell voltage degradation was reversible, i.e. the cell voltage recovered after the humidification was stopped (see Figure 1, as example and Figure 2 for values). It appeared even that the jump back was larger than the initial cell voltage drop. That means not only the initial cell voltage drop but also the long term cell voltage degradation during the ~1500 h period in humid air was reversible, at least to a certain degree.

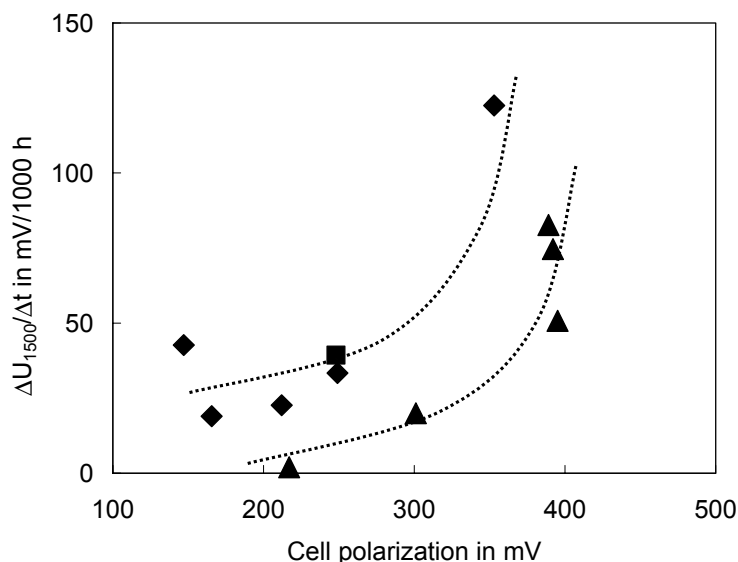


Figure 4. Cell voltage degradation rates during aging tests in dry (triangles: 750°C) or humid air (rhombs: 750°C and square; 800°C) determined as linear decrease over the ~1500 h aging period (in mV/1000 h) as function of cell polarization.

Micro-structural Analysis

The cells were studied after completion of the aging tests. As the focus was on the cathode, the same strategy as in a previous paper (7) was applied, i.e. the cathode layer was etched away and the remaining electrolyte surface was analyzed. In Figure 5, the electrolyte surface of a reference cell tested in dry air and of a cell tested in humid air is shown.

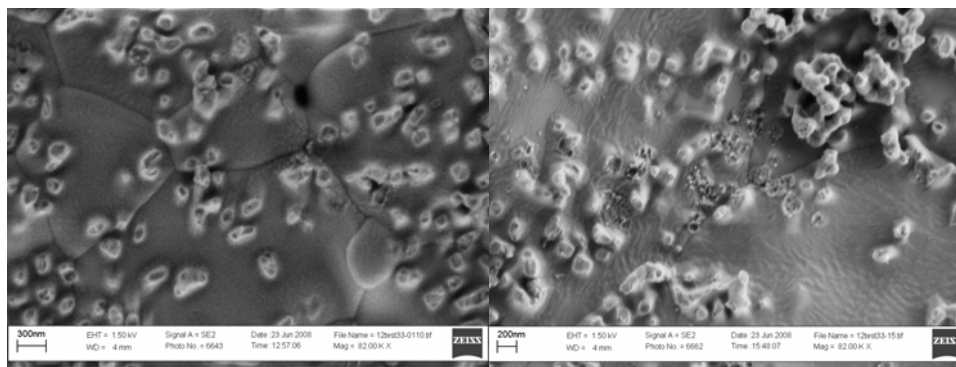


Figure 5. Electrolyte surface after removal of cathode layer, left: cell tested in dry air and right: cell tested in humid air (12test33, see Table I), magnification 82 K.

The electrolyte grains are visible and on top of them the imprints left by the LSM cathode particles (craters). Furthermore, cathode YSZ particles are seen as protrusions. The comparison between the two tested cells reveals significant differences at the cathode/electrolyte interface due to the humid air conditions. These cells show for example the formation of ripple-like structures, randomly distributed along the cathode/electrolyte interface and furthermore a flattening of crater structures representing contact points between LSM cathode and YSZ electrolyte. Generally, the effects were the same as observed for cells tested in dried air under harsh operating conditions over 1500 h, i.e. high current density at 750°C, probably more pronounced when the air had been humidified, in particular the ripple like structures.

The aging tests showed a reversible effect of the humidification of air on the cell voltage. Therefore, the significant structure changes observed on the aged cells after test, such as the ripple-like structures, do not seem to affect the electrochemical performance. That means also, the additional (reversible) aging in humid air is due to another reason.

The cells were therefore further analyzed, this time with focus on the presence of foreign phases around the interface. A cell was quenched, i.e. shut down in humid air. In the subsequent micro structure analysis, it appeared that impurities were concentrated around the interface region. The hypothesis is therefore to relate the degradation effect under humid air and polarization to impurities. In steam and under polarization, impurities in the materials become more mobile and could concentrate around the three-phase boundary points, thereby decreasing the performance. When the humidity is removed, these impurities could return to their original, less detrimental locations.

Improved Cell

The cathode/electrolyte interface thus seems to be a determining part of the cell for the durability in both dried and humid air under polarization and the operating conditions applied in this study. It was therefore attempted to improve this interface by depositing a LSM/YSZ cathode with smaller and more evenly distributed particles at the interface, in order to decrease the ‘polarization per particle’. In Figure 6, the electrolyte surface is shown for an optimized cell after removal of the cathode in comparison to a reference (standard) cell. Two features were improved: the coverage of the surface with cathode

particles; void areas as seen in the standard cell are covered with cathode in the improved cell. In addition, the craters appeared smaller, reflecting smaller cathode particles.

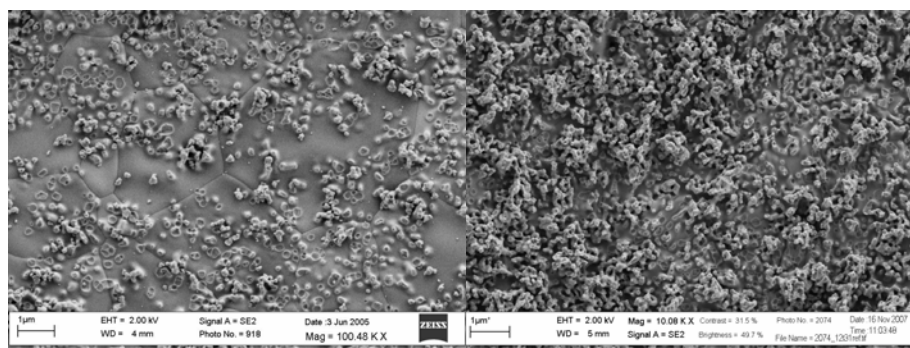


Figure 6. Electrolyte surface after removal of cathode layer, left: reference (standard) cell before testing and right: optimized cell before testing.

In Figure 7, the results of aging tests on a standard and an improved cell in humid air at 750°C and 0.5 A/cm^2 are shown (note that the air utilizations were higher than in the previous tests: 50% on the standard and 70% on the improved cell – the starting cell voltages were the same for both cells). The humidification of air was stopped after ~ 580 h for the standard cell; thereafter the already mentioned immediate recovery of cell voltage occurred. During test of the optimized cell, the humidity was interrupted for about 100 hours (see braces in Figure 7).

Indeed, a cell with an in this way improved LSM/YSZ-cathode / YSZ electrolyte interface proved to be significantly more durable in humid air at 750°C , even over more than 2000 hours (see Figure 7). The improvement factor was ~ 10 in regard to the cell voltage degradation rates.

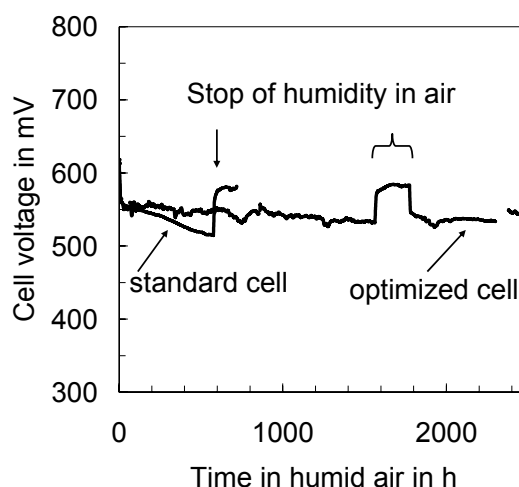


Figure 7. Durability tests in humid air ($\sim 4\%$) on a standard and optimized (improved cathode/electrolyte interface) cell at 750°C , 0.5 A/cm^2 , synthesis gas fuel with 75% fuel utilization, 50% air utilization on the standard and 70% on the optimized cell. Both cells had been long-term tested before the period under humid air, the standard cell for 1800 hours and the optimized cell for 2300 hours. The time scale was normalized to zero at the start of humidification of the air.

Conclusions

The durability study of anode supported cells in humid air showed that these cells can be operated successfully in ~4% humid air at technologically relevant conditions. Humidity has an immediate effect on the cell voltage and a long-term effect, both being reversible under the conditions applied in this study and probably related to the segregation of materials impurities to the three-phase boundary areas in humidity and under polarization. Permanent micro-structural changes observed in particular after aging in humid air (ripple-like structures on the electrolyte surface) do not seem to affect the performance (cell voltage) to a larger extent.

The degradation rate of the cell voltage is affected by introducing humidity in air mainly at the lower operating temperatures of 750°C and high current densities (0.75 A/cm²). These are also the conditions that cause degradation in dried air as well and are related to cathode processes. Increasing the operating temperature to 850°C and decreasing the current density mitigate the effect of humidity in air. Furthermore, the tolerance of cells with LSM-YSZ cathodes can be significantly improved by having an optimal interface between cathode and electrolyte. Such improved cells can even operate without significantly increased cell voltage degradation rates at 750°C and high current density.

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